



IN THE UNITED STATES PATENT
AND TRADEMARK OFFICE

Applicant(s): Tatsuo Chiba et al

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For: PHOTOSENSITIVE ELEMENT, PHOTOSENSITIVE ELEMENT ROLL, PROCESS FOR THE PREPARATION OF RESIST PATTERN USING THE SAME, RESIST PATTERN, RESIST PATTERN LAMINATED SUBSTRATE, PROCESS FOR THE PREPARATION OF WIRING PATTERN AND WIRING PATTERN

Art Unit: 1756

Examiner: Daborah Chacko-Davis

Honorable Commissioner of Patents
and Trademarks
Washington, D.C. 20231

DECLARATION UNDER 37 CFR 1.132

SIR:

I. I, Tatsuya Ichikawa, a second inventor of this case, declare and say as follows.

I am one of the joint inventors of the present U.S. Patent Application as identified above and understand the English language. I studied the Official Action dated March 3, 2007 received in the parent application.

In order to clarify that the present invention is not obvious over the invention of Sato (U.S. Patent No. 5,648,159) in view of Kimura et al. (U.S. Patent No. 6,207,345 B1), I have conducted comparative experiments as mentioned below under my supervision.

II. Comparative experiments

An object of the experiments is to show the superiority of the photosensitive element according to the present invention to those using subject matter of Kumara and Sato, namely, those which do not contain any bisphenol A type (meth)acrylate compound as a photopolymerizable compound and uses comprising a biaxially oriented laminated polyester film of which an outermost surface layer on at least one side thereof contains particles having an average particle diameter of 0.01 to 3.0 μm and has a center line average roughness of not less than 0.005 μm and a maximum height of less than 1.5 μm , and which has a haze of not more than 1.5%.

Example 1 and Additional Comparative examples 1 to 7

The resulting solutions of the photosensitive resin composition A to c as shown in Tables 3 to 5 are uniformly coated on a support films A to C (biaxially oriented polyethylene terephthalate each having a resin layer containing fine particles on one surface thereof with haze of 0.01 to 2.0) and are dried in an oven with internal air circulation at 100°C for 10 minutes to obtain respective photosensitive elements. The film thickness of the photosensitive resin composition layers after drying are 20 to 40 μm as shown in Tables 1 and 2.

Next, a copper surface of a copper-clad laminated board (MCL-E-61, trade name, available from Hitachi Chemical Co., Ltd., Japan) which comprises a glass-epoxy material on which copper foils (each having a thickness of 35 μm) had been laminated on the both surfaces thereof is polished by using a polishing machine (manufactured by Sankei K.K., Japan) having a brush corresponding to #600, washed with water and dried with air stream. The resulting copper-clad laminated board is heated to 80°C, and the above-mentioned photosensitive resin composition layer is laminated on the copper surface at 120°C

and 0.4 MPa (4 kgf/cm²).

Thereafter, exposure is carried out by using an exposure machine (model: HMW-201B, trade name, manufactured by Orc Seisakusho Co., Japan) having a 3KW ultra high pressure mercury lamp in such an energy dose that the number of remaining step grades after development became 8.0, using a photo tool having a Stofer 21 grade step tablet as a negative mask and a photo tool having a wiring pattern with a line/space of 10/400 to 250/400 (resolution, unit: μm) as a negative mask for evaluating adhesive property. Then, the support film is removed, and development is carried out by spraying a 1.0% by weight aqueous sodium carbonate solution at 30°C.

Here, the adhesive property is evaluated with the minimum value of the line width among the fine lines adhered to the substrate after the development. The smaller numerical value obtained by the adhesive property test means better results.

Thereafter, by using a comb-shaped pattern with 5 μm , a resist pattern is prepared in the same manner as that of the adhesion property test, and resolution (μm) is evaluated from the remaining resist pattern. The smaller numerical value obtained by the resolution test means better results.

Next, exposure is carried out with the above-mentioned energy dose and a line width/space width of 50 μm /50 μm followed by development with optimum development time (additional comparative examples 1 to 4: 50 seconds; 5 and 8: 20 seconds; 6: 30 seconds; 7: 40 seconds), and the shape of the resulting resist pattern is observed by a scanning type electron microscope to evaluate the nick property (a side wall unevenness of a resist pattern) on the side surface of the resist pattern.

A side wall unevenness of a resist pattern is a state in which the shape of a resist pattern of the side wall is not flat but unfavorably shaped like serrated jaw tips. The pits and projections occurred in a side wall of a resist pattern is desirably as shallow as possible.

Deep: The case where unevenness of the side surface's nick exceeds 2 μm .

Shallow: The case where unevenness of the side surface's nick is not more than 2 μm .

The results are shown in Tables 1 and 2. And SEM photos of additional comparative examples 5 to 7 and example 1 of the present invention are shown in Figures 1 to 4.

Table 1

Sample	Additional Comparative Examples			
	1	2	3	4
Photosensitive resin composition	A	A	B	B
Thickness of photosensitive resin composition layer (μm)	40	20	40	20
Support film	A	A	A	A
Resolution (μm)	50	35	45	35
Adhesiveness (μm)	40	25	40	25
Side wall flatness*1)	Shallow	Shallow	Shallow	Shallow

*1) Copper plating (line/space=30/30 (μm), thickness of plating: 10 μm)

Table 2

Samples	Additional Comparative Examples 5	Additional Comparative Examples 6	Additional Comparative Examples 7	Example 1 of the present invention
Photosensitive resin composition	C	C	C	C
Thickness of photosensitive resin composition layer (μm)	20	30	40	20
Support film	B	B	B	C
Resolution (μm)	20	30	45	15
Adhesiveness (μm)	15	20	35	15
Side wall flatness*1)	Deep See Fig. 1	Deep See Fig. 2	Shallow See Fig. 3	Shallow See Fig. 4

Photosensitive resin composition A is prepared according to Table 3 (Preparation example 1 of Kimura et al.)

Photosensitive resin composition A is prepared according to Table 4 (Preparation example 2 of Kimura et al.)

Photosensitive resin composition C is prepared according to Table 5 (Preparation example 1 of the present invention)

Support film A: a biaxially oriented laminated polyester film (thickness: 16 μm) of which an outermost surface layer on at least one side thereof contains particles having an average particle diameter of 0.1μm and has a center line average roughness of 0.01 μm and a maximum height of 0.2 μm, and which has a haze of 0.4%*.

Support film B: a polyethylene terephthalate film without a resin layer containing fine particles, and which has a haze of more than 2.0 (G2-19).

Support film C: A2100-16 available from Toyo Boseki K.K., Japan which is a support film used in example 1 of the present invention.

*: Please note that this film is not the film of Sato but it is a film very similar to the film of Sato. The film of Sato was difficult to acquire directly, therefore, this similar film is used instead. However, the use of Support film A in place of Sato's film should not substantially effect the results of the test because Support film A meets all the essential physical characteristics of Sato's film as described in the Abstract of Sato.

Table 3 Photosensitive resin composition A

Material	Formulation amount
Copolymer of methacrylic acid/methyl methacrylate (weight ratio: 25/75, weight average molecular weight: 75,000)	60 parts by weight
Tetrapropylene glycol diacrylate	40 parts by weight
Diethylaminobenzophenone	0.2 part by weight
Benzophenone	5 parts by weight
Crystal Violet	0.003 part by weight
Methyl ethyl ketone	100 parts by weight

Table 4 Photosensitive resin composition B

Material	Formulation amount
40% by weight solution of methacrylic acid/ methyl methacrylate/ethyl acrylate/ethyl methacrylate copolymer (weight ratio: 22/45/27/6, weight average molecular weight: 75,000, acid value of solid component: 144) in methyl cellosolve/toluene (weight ratio: 6/4)	150 parts by weight (solid component: 60 parts by weight)
2,2'-Bis(4-(methacryloxy)pentethoxy)phenyl)propane	30 parts by weight
γ -Chloro- β -hydroxypropyl- β '-methacryloxyethyl-o-phthalate	10 parts by weight
1,7-Bis(9,9'-acridinyl)heptane	0.4 part by weight
N,N'-tetraethyl-4,4'-diaminobenzophenone	0.05 part by weight
Leuco Crystal Violet	0.5 part by weight
Marachite Green	0.05 part by weight
Tribromomethylphenylsulfone	1 part by weight

Table 5 Photosensitive resin composition C

Material	Formulation amount	
Component (A)	40% by weight solution of methacrylic acid/methyl methacrylate/styrene copolymer (weight ratio: 25/50/25, weight average molecular weight: 70,000, acid value: 163 mg KOH/g) in toluene/methyl cellosolve (weight ratio: 4/6)	150 g (solid component: 60 g)
Component (B)	2,2-Bis(4-(methacryloxy)pentethoxy)phenyl)propane	30.0 g
	γ -Chloro- β -hydroxypropyl- β '-methacryloxyethyl-o-phthalate	10.0 g
Component (C)	2-(o-Chlorophenyl)-4,5-diphenylimidazole dimer	3.0 g
	N,N'-Tetraethyl-4,4'-diaminobenzophenone	0.15 g
Other Components	Leuco Crystal Violet	0.5 g
	Marachite Green	0.05 g
	p-Toluenesulfonic amide	4.0 g

Consideration of experimental results

Evaluations of the experimental results shown in Table 1 are made under the following standard:

Resolution:

Smaller than 20 μm :	Good
Over 20 μm but smaller than 30 μm :	All right (OK)
Over 30 μm :	Bad

Adhesiveness:

Smaller than 20 μm :	Good
Over 20 μm but smaller than 30 μm :	All right (OK)
Over 30 μm :	Bad

A side wall unevenness of a resist pattern:

Shallow:	Good
Deep:	Bad

As can be seen from Tables 1 and 2, it is clear that additional comparative examples 1 and 3 are a combination of the support film corresponding to Sato with the photosensitive resin layer composition described in the example of Kimura et al. Both results showed shallow unevenness in side wall of resist pattern, but inferior in resolution and adhesiveness. When thickness of photosensitive resin layer are made to be 20 μm as in additional comparative examples 2 and 4, which thickness is the same as the thickness of the present invention, resolution and adhesiveness are little improved but not improved enough to satisfy the property level required in the field of a semiconductor package.

Additional comparative examples 5 to 7 are the examples which compare properties with the change of thickness in a

combination of conventional support film with the photosensitive resin layer composition of the present invention.

The results showed that thinning of thickness gives improvement in resolution and adhesiveness but become worse for side wall unevenness of resist pattern.

It is concluded that no problem of side wall unevenness of resist pattern is caused when photosensitive resin layer is thick although it is inferior in resolution and adhesiveness. On the other hand, thinning of the photosensitive resin layer thickness makes better resolution and adhesiveness but problem of side wall unevenness of resist pattern starts to generate (See Figures 5 to 7).

The inventors of the present invention have studied and reviewed various factors including composition changes of photosensitive resin in order to overcome these problems but it was not possible to overcome side wall unevenness of resist pattern. The inventors dedicated in studying and succeeded in improvement of side wall unevenness of resist pattern by selecting the support film of the present invention (see Figure 8), thereby accomplished the present invention.

III. Conclusion

I believe that the above results would indeed be surprising and could never be expected from the description of the cited references. Thus, I do not believe that the present invention is obvious over Sato and Kimura et al.

IV. I further declare that all statements made herein of my own knowledge are true and that all statements made in information and belief are believed to be true; and further that these statements are made with the knowledge that willful

false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001, of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: 27th June 2007

T. Ichikawa

Tatsuya ICHIKAWA